

**PROCESS FOR COATING SUBSTRATES WITH CATALYTIC MATERIALS****Claim of Benefit of Provisional Application**

5 Pursuant to 35 U.S.C. §119, the benefit of priority from provisional application 60/141,729, with a filing date of June 30, 1999, is claimed for this non-provisional application.

**Origin of the Invention**

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The invention described herein was jointly made by employees of the United States Government and contract employees during the performance of work under a NASA contract which is subject to the provisions of 35 USC 202 in which the contractor has elected not to retain title.

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**Background of the Invention****1. Field of the Invention**

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This invention relates generally to the process of coating substrates with one or more catalytic components to form a catalyst. It relates particularly to the process of layering one or more catalytic components onto a honeycomb monolith to form a carbon monoxide oxidation catalyst which combines CO and O<sub>2</sub> to form CO<sub>2</sub>, or alternatively, a volatile organic compound oxidation catalyst which combines the compound and O<sub>2</sub> to form CO<sub>2</sub> and H<sub>2</sub>O.

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**2. Description of the Related Art**

The catalytic conversion of carbon monoxide to carbon dioxide in the presence of oxygen is useful to a number of fields. Applications in which CO oxidation catalysts

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may be successfully employed include the following: (i) catalytic removal of CO in air-purification systems, especially for enclosed spaces; (ii) removal of CO in filter canisters, and the like, for personal breathing apparatuses; (iii) removal of CO from combustion products of cigarettes; (iv) removal of CO from exhaust gases expelled from gasoline- and diesel-powered internal combustion engines; and (v) catalytic conversion of dissociation products in CO<sub>2</sub> lasers to maximize laser power and life, and minimize laser weight, size, and engineering complexity. Each of these and other applications require a different embodiment of a CO oxidation catalyst and place a different emphasis on one or another quality. Thus, a catalyst for an air-purification system necessarily must have a high throughput, while a catalyst for an internal combustion engine requires the capacity to operate over a broad temperature range, and cost per unit takes on greater significance in the cigarette application.

Improvements in CO oxidation catalysts are continually being sought to increase the versatility, effectiveness, durability, activity, and operating life of the CO oxidation catalyst.

Several patents, e.g., U.S. Pat. Nos. 4,912,082 and 4,991,181 to Upchurch and U.S. Pat. Nos. 4,818,745 and 4,808,394 to Kolts, disclose compositions useful to CO<sub>2</sub> laser applications. During the operation of a CO<sub>2</sub> laser, CO<sub>2</sub> decomposes into CO and O<sub>2</sub> in the laser's electrical discharge zone. The concentration of the dissociation products increases throughout the laser's operation, while the

concentration of  $\text{CO}_2$  correspondingly decreases. Both the loss of  $\text{CO}_2$  and the build-up of  $\text{O}_2$ , which scavenges electrons from the  $\text{CO}_2$  molecules, significantly reduce the lasing power and degrade the performance of the laser. This problem may be addressed either by continually replacing the dissociation products with fresh  $\text{CO}_2$  during the laser's operation or by using an ambient temperature CO-oxidation catalyst. The former is expensive and, especially for most airborne and space applications, unworkable because of the weight penalty. Hence, the latter is preferred, but the catalyst must have an extended activity life for most applications.

In U.S. Pat. Nos. 4,994,247 to Tooley and 5,017,357 to Kolts, CO-oxidation  
30 catalyst compositions are disclosed which are suitable for a number of applications

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including the minimization of CO in tobacco smoke; removal of CO for personal breathing masks, e.g., those worn by miners; and CO<sub>2</sub> laser applications. Matsuyama, in U.S. Pat No. 4,117,082, and Harrison, in U.S. Pat. No. 5,051,393, disclose CO-oxidation catalyst compositions developed for use in minimizing carbon monoxide and/or unburnt hydrocarbons from vehicle exhaust. U.S. Pat No. 4,639,432 to Holt discloses CO-oxidation catalyst compositions directed towards the previously stated problems and also towards air-purification or ventilation systems for the removal of CO from confined spaces, especially where traditional ventilation methods are difficult or unfeasible. Examples include nuclear submarines and areas around welding equipment.

In many applications it is also highly desirable, if not necessary, to remove hydrocarbons and other volatile organic compounds from the air via oxidation to CO<sub>2</sub> and H<sub>2</sub>O without the aid of filters and with minimal heating of the catalyst. By way of example, there has been a long-standing need for a method to remove volatile organic compounds from indoor air, i.e., breathable air in enclosed spaces such as homes, automobiles, airplanes, ships, boats, and industrial plants where there may be high concentrations of said compounds. Other significant long-standing needs include the need to purify compressed air and other oxygen-containing gases, as well as the employment of personal safety masks in the removal of volatile organic compounds from the atmosphere. There has also been a need for such a method in selective chemical sensors and catalytic converters for combustion processes, including internal combustion engines which utilize gasoline, diesel, natural gas, and alcohol fuels.

Considering the range of applications and requirements specific to each, there is an ever present need to develop new, effective oxidation catalyst compositions and/or improved processes for preparing effective oxidation catalyst compositions. Any improvement which increases the versatility, effectiveness, durability, activity, and/or operating life of the catalyst or the process for making such, satisfies this need.

Supported catalysts - specifically, supported carbon monoxide oxidation catalysts - may be prepared by (i) coating a support with "catalytic paint"; (ii) impregnation with precipitation agents in one or multiple steps; (iii) impregnation

followed by calcination or firing; and (iv) “anchor coating” where a dense, less penetrable support is first coated with another non-catalytic, more penetrable substance to provide a high surface area receptive to further impregnation by catalytic components.

Coating supports with “catalytic paint” is analogous to the method of pill coating employed by the pharmaceutical industry. Cores of support material are placed in a rotating drum and a “paint” slurry is added to coat the cores. The thickness of the catalyst coating is determined by the amount of “paint” added. A serious disadvantage of this method is that the catalyst material may peel from the support (technically termed “spall”) resulting in (i) a catalytically inert support and (ii) spalling powder which will likely travel and gather downstream of the catalyst bed to distort or plug the gas flow.

Impregnation methods generally include suspending the support in a solution of the catalytic material and slowly precipitating the catalytic material onto the support or impregnating the support with the precipitant and then using a technique to force precipitation of the catalytic components immediately on the surface. Three major disadvantages are associated with impregnation methods. First, impregnation via precipitating agents may leave unwanted residues. These residues can decompose to form undesirable gases in levels unacceptable for air purification applications. Second, the catalyst precursor materials used often contain catalyst poisons, e.g. chloride, which limit the activity and effectiveness of the catalyst. Third, impregnation - and “anchor coating” and washcoating - often rely on high temperature firing or calcination to complete the coating process. Exposure to high temperatures will reduce the surface area and lower the activity of the resultant catalyst. In addition, impregnation methods involve extra steps which increases the cost of production.

Catalysts may also be prepared in powder form. Unsupported catalysts suffer from dusting, which is particularly vexing for high throughput applications. In addition, they provide poor dispersion of catalytic materials which both reduces the effectiveness and increases the cost of the catalyst for a given application.

30 There is an ever present need for new, improved processes for the preparation

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of effective oxidation catalyst compositions. Improvements in the process which increase the versatility, effectiveness, durability, activity, and/or operating life of the oxidation catalyst satisfy this need. There is a long-standing need for an improved, efficient process of coating substrates with catalytic materials.

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### Summary of the Invention

The present invention is a process for forming catalysts by coating substrates with one or more catalytic components and comprises the following sequence of steps.

- 10 First, the substrate is infused with an excess of solution having a starting material comprising a catalytic component precursor, where the thermal decomposition product of the catalytic component precursor is a catalytic component. Second, the excess of the solution is removed from the substrate, thereby leaving a coating of the catalytic component precursor on the surface of the substrate. Third, the coating of the
- 15 catalytic component precursor is converted to the catalytic component by thermal decomposition. This is achieved by heating the coated substance to approximately 300 degrees Celsius, where the rate of heating is controlled to prevent high temperature calcination of the catalytic component precursor and where any remaining starting material is thermally decomposed, oxidized, and/or volatilized without high
- 20 temperature calcining, thereby leaving only the catalytic component and no residues on the substrate surface. Finally, the coated substance is etched to increase the surface area. This can be achieved by submerging and refluxing the coated substance in a dilute solution of nitric acid.

- The first three steps of the above process are repeated in order to successively
- 25 layer more than one catalytic component on the substrate. In addition, the first step may be improved by infusing the substrate with an excess of solution by vacuum deaeration, and the second step may be improved by removing the excess of the solution by draining away and/or evaporating off the excess of the solution. If the catalyst is "cured" by heating in an atmosphere of a reducing gas prior to its use, its
- 30 activity may be substantially improved even further. The potential reducing gases

include, but are not limited to, carbon monoxide and hydrogen.

Beneficial results are achieved where the process is used to form a catalyst consisting of a substrate and three catalytic components; wherein the substrate is selected from the group comprising ceramics, glass, metals, and fabrics; wherein the ceramic substrate is selected from the group comprising beads, pellets, and monoliths; wherein the first catalytic component is a metal oxide selected from the group comprising manganese oxide, copper oxide, and tin oxide; wherein the second catalytic component is a metal oxide, where this metal oxide is used as a promoter to increase the activity or catalyzing rate of the catalyst, and is selected from the group comprising the oxides of vanadium, chromium, copper, cobalt, manganese, nickel, or iron; and wherein the third catalytic component is a noble metal selected from the group comprising platinum, palladium, rhodium, iridium, ruthenium, osmium, and gold. Especially beneficial results are achieved where the process is used to form a catalyst consisting of a honeycomb monolith ceramic substrate successively coated with tin oxide, iron oxide, and platinum.

### Description of the Drawings

**Fig. 1** is a graph representing the effect of  $\text{HNO}_3$  etching after  $\text{SnO}_2$  loading on the conversion efficiency of  $\text{Pt}/\text{SnO}_2$  for CO oxidation

### Example

SnEH was used to coat all the catalyst samples presented. SnEH is a liquid at room temperature. Acetone can be used to reduce the viscosity and ultimately provide thinner layers or perhaps micro-droplets of SnEH on the surface of the substrate once the acetone has evaporated. Each substrate was vacuum deaerated in SnEH either pure or diluted with acetone. Deaeration facilitates exchange of trapped air in the pores of the monolith with the desired solution insuring a thorough coating with the starting material. After deaeration, the excess solution was shaken, drained or blown from the substrate. Next the SnEH-coated substrate was placed in a muffle furnace and

heated from ambient temperature to 200°C at 1°C/min and held for 3-6 hours and then heated to 300°C at 1°C/min for 2-6 hours to decompose the SnEH to tin oxide and remove residual organic material, respectively. The above steps were repeated until the desired loading of tin oxide was obtained. The SnO<sub>2</sub>-coated substrate was etched

5 to increase the surface area of the  $\text{SnO}_2$  layer which ultimately provides better dispersion of the noble metal. The  $\text{SnO}_2$ -coated substrates were submerged in 1.5 to 1.6 M nitric acid and heated to near boiling. Etching time varies depending on the desired surface area of the  $\text{SnO}_2$ -coated substrate. Once etched, the substrates were rinsed with hot DI water to remove any residual nitric acid. Finally the substrates were  
10 placed into a muffle furnace and dried at  $100^\circ\text{C}$  for 1 hour then to  $250^\circ\text{C}$  for 2 hours to decompose any nitric acid. CO oxidation activity improved 300-400% for the same amount of noble metal when compared to non-etched substrates or substrates etched prior to the application of the first catalytic component.

The present invention has been described in detail with respect to certain preferred embodiments thereof. However, as is understood by those of skill in the art, variations and modifications in this detail can be made without any departure from the spirit and scope of the present invention as defined in the hereto-appended claims.

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